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Opportunities in Processing of Metal Resources in South East Europe

held in conjunction with the

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eit RawMaterials

OPMR – OPPORTUNITIES IN PROCESSING OF METAL RESOURCES IN SOUTH EAST EUROPE

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PREFACE

Dear Delegates, Colleagues, Authors and Guests,

The organizing committee from Montanuniversitaet Leoben, University of Miskolc and the Regional Innovation Center Leoben, supported by the Austrian Society for Metallurgy and Materials (ASMET), welcomes our participants to the OPMR2016 and the 5th ESEE Dialogue conference.
The conferences are organized to bring together the members of the international scientific community with industry from the fields of mineral processing, extractive metallurgy and recycling focused on the East South East European (ESEE) region at one platform. This offers the opportunity to expand our community's knowledge and provides an insight into the challenges currently addressed by industry.
The papers published in this proceedings book were submitted, revised and approved by the Scientific Committee to be presented and published at the conference, taking place in Budapest, Hungary between 28th and 30th November 2016.
The editors of this proceedings book wish to thank all the reviewers that, being part of the Scientific Committee of the conference, gave input to the reviewing process.

The organizing committee

ESEE STANDS FOR EAST- AND SOUTH- EAST EUROPE, AND ESEE SOUNDS EASY!

From a political point of view (cohesion, regional development, "Candidate Countries" and "Potential Candidates") and from an economic point of view (security of supply with raw materials, economic value and employment) the ESEE Region is highly relevant. It is of particular interest due to its unique geological potential and unique potential on secondary raw materials (overall and especially for some critical minerals). Our overall target is to raise interest for the ESEE region's raw materials potentials by creating an ESEE community open for every interested and competent RawMaterial partner of the ESEE region. The idea is to bring KIC EIT RawMaterials partners to the ESEE region and to bring ESEE partners to the KIC.

EIT RawMaterials brings together partners from academia, industry and research within the raw materials sector in so called Knowledge and Innovation Communities (KICs) in order to boost its growth and innovation and to strengthen research and knowledge sharing. The network aims to provide new opportunities for collaboration and access to research facilities for raw material experts from different backgrounds or disciplines. The network makes it possible to cover all stages of the complex raw materials process cycle, from exploration and extraction via processing and metallurgy up to recycling and substitution. The human expertise and the research structures of the institutions raise the network's overall potential to meet current and future challenges concerning raw materials in a comprehensive and integrative way, with a special focus on sustainability.

In cooperation with the OPMR Conference the floor is given to experts from the thematic areas in Metallurgy and Mineral Processing focussing on activities and developments in the ESEE Region. As for the further cooperation within the KIC EIT RawMaterials and RIC ESEE network, this conference is seen as a starting point for more detailed activities within the mentioned region.

A special thank you should be placed here to the Scientific Committee, as well as the organizing institutions such as Montanuniversitaet Leoben, University of Miskolc, Chair of Non-Ferrous Metallurgy, ASMET and the team of RIC ESEE.

Let's meet to create a successful future of common project, activities and partnership of Raw Materials in the ESEE Region

TOPICS

- Mineral deposits in the ESEE Region: case studies
- Mineralogical characterization of raw materials
- The mineral inventory of the ESEE Region
- Innovations in Mineral Processing
- Mineral Processing Plants in the ESEE Region: Case Studies
- Instrumentation and Automation in Mineral Processing

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Novel methods of extracting pure metals by the application of chloride hydro-electrometallurgy

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Abstract. Pursuing one of the main convictions of the Institute of Metallurgy at the University of Miskolc, we have found good opportunities of applying hydro-electrometallurgical methods extracting metallic values from waste materials produced. The equilibrium conditions in the chloride solutions were examined by thermodynamic simulation and the processes were investigated by laboratory experiments. The relatively large amounts of dross generated by the use of lead-free soldering alloys was an ideal raw material for producing pure tin by an aqueous electrorefining procedure in HCl-$SnCl_2$ media. The proper anodic dissolution of tin, the stability in the electrolyte solution and the required cathode purity was ensured by optimised conditions in terms of solution composition and electrolysis parameters. Processing the most common Sn-Ag-Cu waste materials implied the generation of an equally valuable silver containing by-product easily removed as a non-dissolved sludge. A chloride hydrometallurgy based process was also devised for the processing of this sludge. We have also processed acidic copper chloride solutions originating from the etching of printed circuit boards. In this case, high purity copper could be deposited at the cathode in a cell equipped with a cation exchange membrane separation of the inert anode. Current efficiencies were found strongly affected by the distribution of copper ions among different valence states and chloride complex structures, and also by the current densities. The purity of the produced metal could be enhanced by applying anion-exchange separation to purify the chloride solution before feeding it into the cathode compartment. A method has been devised also for recovering iron, zinc and hydrochloric acid from spent pickling liquors generated by the preparatory step of hot dip zinc coating. In this case anion-exchange is vitally important to remove zinc from the chloride solution before electrodepositing iron in a cell equipped with a cation exchange membrane separation and a hydrogen diffusion anode. Although the efficiency is sensible to acid concentration, the produced iron is of super purity.

1. Introduction

Modern industrial technologies produce various waste materials that can be considered valuable raw materials for metals extraction if there are efficient and environmentally friendly metallurgical methods available. One of the most important examples is the dross obtained from the wave soldering technology used in the production of high quality electronic devices and from the tin coating technology used for producing the electric contacts for inductivity coils and diodes. The mandatory change for lead-free soldering implies the generation of more dross because the alloy is more reactive towards oxygen and to copper [1]. The most common alternatives are tin based alloys containing Ag and Cu [2], requiring the molten bath to be regularly refreshed with copper-free tin and silver. No direct technology has been available for recycling, thus long transportation and conventional tin metallurgy is currently the only available solution. However, it has been shown [3,4] that pure tin can be recovered by a straightforward electrorefining method applying $SnCl_2$ - HCl media near the production sites. The known commercial practice uses sulphate solutions containing a substantial amount cresylic-phenylic sulphonic acid and β-naphtol or other organic additives for solution stability and controlled crystal growth. On the other hand, hydrochloric acid may offer high solubility and stability by chloro-complex formation, which in fact may also contribute with some inhibiting effect in electrocrystallization. In order to avoid the expensive ingredients and to be able to produce high purity metal, we aimed to use dilute HCl solutions of tin,

without any additives. Purity of the cathode tin may be higher than satisfactory for recycling to the soldering baths to control the composition, or to be used in the food industry. There have been two major difficulties related to the electrorefining of tin in pure acidic aqueous solutions. One of them is the dendritic morphology of the tin crystals deposited at the cathode surface and the other is providing the optimum conditions for the dissolution of the anode [3,4]. If tin is dissolved overwhelmingly at the highest oxidation state and it becomes predominant in the solution, stannic acid type precipitation may disrupt normal procedure. As the tin deposition is generally characterized by the formation of long dendrites [5], the rate at which diffusion can supply the ions to the cathode surface must be considerably lower than the rate of charge transfer. Efficient solution agitation, however, is difficult at the surface of the electrode and it may disperse unwanted particles from the anode slime into the electrolyte. Another way to tackle this difficulty could be the application of periodically reversed or interrupted current, or electrodeposition with micro-scale current impulses. These techniques have really been proved [5] to influence beneficially the crystal form to some extent, but an adequately dense cathode deposit could only be achieved by mechanical compression [5,6]. Conditions allowing a long term operation recovering pure tin from the soldering dross required fundamental studies of the chemical and electrolytical characteristics, followed by optimization of the parameters.

The key functional devices of modern electronic equipment are operated on a printed circuit board (PCB). Its manufacturing involves the removal of a relatively large amount of copper from the surface coating of the carrier plate by chemical dissolution. For fast and large scale copper removal divalent copper in chloride solutions is used as an aggressive reagent and the resulting monovalent copper is oxidized subsequently. A strong (~ 3M) hydrochloric acid background is applied for stabilizing the dissolved species in chloride complex ions. As the copper concentration gradually increases some of the solution needs to be replaced by pure HCl. Therefore a $CuCl_2$ – HCl spent liquor of high copper concentration (~160 g/dm^3) is continuously generated. This may lend itself to direct electrowinning, especially because the impurities are at relatively low levels. Only zinc (~ 300 mg/dm^3) and iron (~ 25 mg/dm^3) should be considered for preliminary removal if super high purity cathode copper – of considerably higher than ordinary value - is to be produced. This may be carried out by some special solution purification by applying anion exchange [7]. In general, divalent copper ions are aggressive against metallic copper if the solution contains sufficiently high concentration of free chloride ions. It is useful for etching, but it also causes low current efficiencies in electrodeposition of copper from chloride solutions [8]. In order to find the workable conditions it was necessary to investigate the states of ions in the chloride solution and to interpret the processes by running electrowinning experiments.

Huge amounts of spent pickling liquors are generated worldwide by the preliminary step of hot dip zinc coating. The hazardous waste solution contains usually 70-140 g/dm^3 iron, up to 40 g/dm^3 zinc and 0.5 – 1 M hydrochloric acid, depending on the level of exhaustion [9]. Although several techniques have been proposed for the purpose of treating these solutions - like neutralization, evaporation, diffusion dialysis, pyrolysis, solvent extraction – none of them are capable of entire utilization, because large amounts of hazardous wastes are produced again and the products can hardly be marketed [9-11]. A suitable electrolysis of pickling solutions can produce iron at the cathode and regenerate HCl in the anode compartment. These products are completely recyclable without any significant discharge. However, the implied electrolytic reactions are often accompanied by side reactions reducing the current efficiency of both the cathodic deposition of iron and the regeneration of HCl. As iron is characterized by a fairly negative standard electrode potential, the effect of acid concentration at the cathode may be of concern and chloride ions should also be prevented to be neutralized at the anode. These requirements could be met by the application of an anion exchange membrane separation between the cathode and the anode compartment and the use of a novel hydrogen diffusion anode instead of the conventional inert one In order to protect the capacity anion exchange membrane allowing the regeneration of hydrochloric acid in the anode compartment and preventing the transfer of hydrogen ions to the cathode, the generally high zinc concentration in the raw hydrochloric solution had to be removed by a preliminary anion exchange separation.

2. Equilibria of the targeted metals in chloride solutions

The difficulty of stabilizing the anodic dissolution of tin in any acidic medium is caused by the incidental generation of Sn(IV) species. In simple acidic aqueous solutions, the predominant oxidation state is determined by the redox potentials of the coupled aquo ions. The Sn^{4+}/Sn^{2+} couple is more positive (+0.147 V) than the Sn^{2+}/Sn one (-0.136 V) therefore Sn^{4+} is reduced and Sn metal is oxidized in a com-proportionation reaction if all oxidation states may exist in contact:

$$Sn^{4+} + Sn = 2Sn^{2+} \tag{1a}$$

Therefore Sn^{2+} is the stable form if metallic tin is in contact with the solution. If free chloride ions are also present, the aquo species may be more or less converted into $[SnCl_x]^y$ chloro-complexes, and reaction (1a) is replaced by the following resultant process:

$$[SnCl_y]^{|4-y|\mathrm{sgn}(4-y)} + Sn + (2x-y)Cl^- = 2[SnCl_x]^{|2-x|\mathrm{sgn}(2-x)} \tag{1b}$$

or in a short notation:

$$Sn(IV) + Sn = 2Sn(II) \tag{1c}$$

As proven by the results of thermodynamic simulation [3] carried out by using the computer program ROCC (Reduction-Oxidation-Chloro-Complexation) [12] and the published stability constants of the chloro-complexes and the standard potentials of the aquo couples [13,14], Fig. 1*a*, shows that the chloride medium enhances reaction (1) and the chloro-complex formation helps stabilizing the preferred divalent Sn(II) state. The stabilization of the dissolved ions may also affect the potential required for cathodic reduction. Figure 1*b* demonstrates that at higher than ~ 0.1 V potential in 1 M HCl, tin may be dissolved primarily as Sn(IV), whereas the required potential to reduce Sn(II) to the metallic state is steeply decreasing with increased Cl^- concentrations (i.e. with decreasing pCl^-).

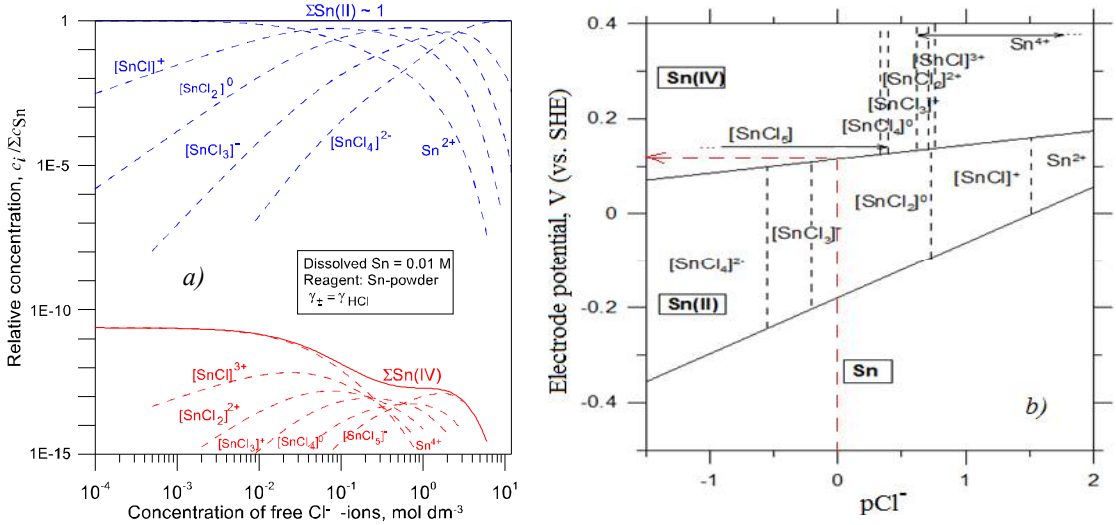

Figure. 1. Equilibrium distribution (a) of Sn among different species in HCl solutions in contact with tin metal, and the potential-pCl^- diagram (b).

Even if the primary reaction of tin dissolution at the anode generates Sn(IV), the loosely adherent anode slime contains enough tin particles, the possible com-proportionation reaction may help to generate the instead of the preferred divalent ions. Reaction (1) has, however harmful consequences at the cathode side, resulting in cathode corrosion. Furthermore, as the finest tin crystals are re-dissolved, the cathode loses active surface area and the local current density may increase, causing hydrogen evolution. Consequently the acid concentration may drop in such regions and the tetravalent tin ions may start precipitating by hydrolysis. The tetravalent Sn (IV) state may also arise by the oxidizing effect

of the ambient air, which process is driven by a high thermodynamic force [3] and the relative position of the curves for Sn(II) and Sn(IV species in Fig. 1a are reversed. However, the rate of this harmful process have been found relatively slow even if air is bubbled into the $SnCl_2$-HCl solution [3]. If Sn(IV) species are present in the solution, they may precipitate by hydrolysis – causing turbidity - as the HCl concentration drops considerably below 1 mol/dm^3 [15], and the formation of hydrated tin-dioxide particles may eventually break up the electrolyte. However, Cl^- activity by forming complexes may stabilize the tin solution.

Copper is different from the most of the other common metals in that the its higher oxidized divalent ion is more stable in ordinary acid solutions. This is because the redox potential of the Cu^{2+}/Cu^+ couple (+0.159 V) is lower than that of the Cu^+/Cu couple (+0.521 V). The conditions prevailing in the chloride solution in contact with a copper surface are demonstrated by the results of Fig. 2, computed with the ROCC software [12] by using the available redox potentials and complex stability data [13,14]. As shown in Fig. 2a, the usually stable Cu(II) species loose their stability and are reduced by metallic copper to the Cu(I)) state if the Cl^- ion concentration exceeds ~ 0.1 M:

$$\mathrm{Cu(II) + Cu = 2Cu(I)} \tag{2a}$$

$$[\mathrm{CuCl}_y]^{|2-y|\mathrm{sgn}(2-y)} + \mathrm{Cu} + (2x-y)\mathrm{Cl}^- = 2[\mathrm{CuCl}_x]^{|1-x|\mathrm{sgn}(1-x)} \tag{2b}$$

Thus similarly to the case of tin, cupric ions can also dissolve copper in contact with chloride solutions effectively. It may have harmful consequences – similarly to the case of tin – at the cathode. In the bulk solution – away from the surface of the copper plate - oxidation of the dissolved Cu(I) ions is possible even by the relatively mild effect of ambient air, demonstrated by Fig. 2.*b*, which entails the danger of current losses during cathodic metal deposition, but the higher oxidation state is not associated with the danger of hydrolytic precipitation in acid media.

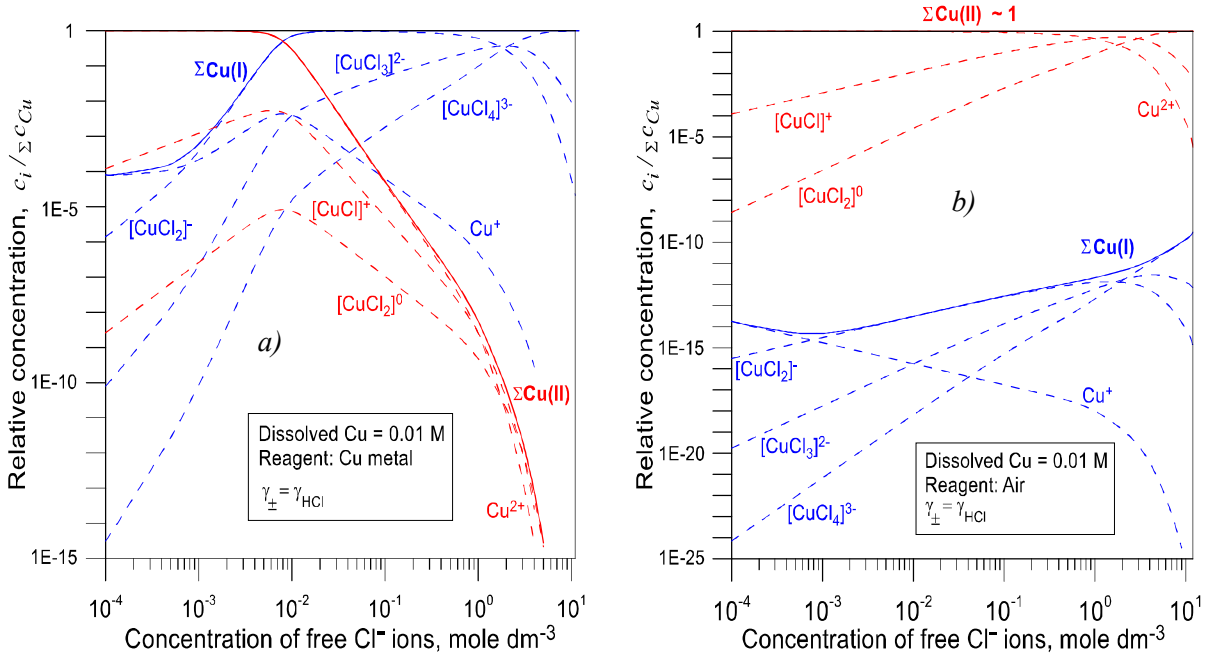

Figure 2. Stability of Cu species in chloride solution contacted with (a) copper, (b) air.

Contrarily to the case of recovering tin from the soldering waste material by electrorefining, the copper content of the spent PCB etching liquor is in the higher valence state, as Cu(II). Therefore, an intensive cathode corrosion is expected right at the beginning of the operation, even if oxidation by air is excluded, which requires careful controlling of the solution and the electric parameters. A further difficulty may arise in the copper chloride solution from the hydrolytic stability of Cu(I) in the chloride solution. As

shown in the E-pCl diagram of Fig. 3, constructed from redox potential and complex stability data [8,13,14], there exists a critical range of medium high HCl concentration combined with the moderate redox potentials where Cu(I) is neither oxidized or reduced, and the complex ion cannot stay stable, causing CuCl precipitation. This range of precipitation is wider at higher total copper concentrations.

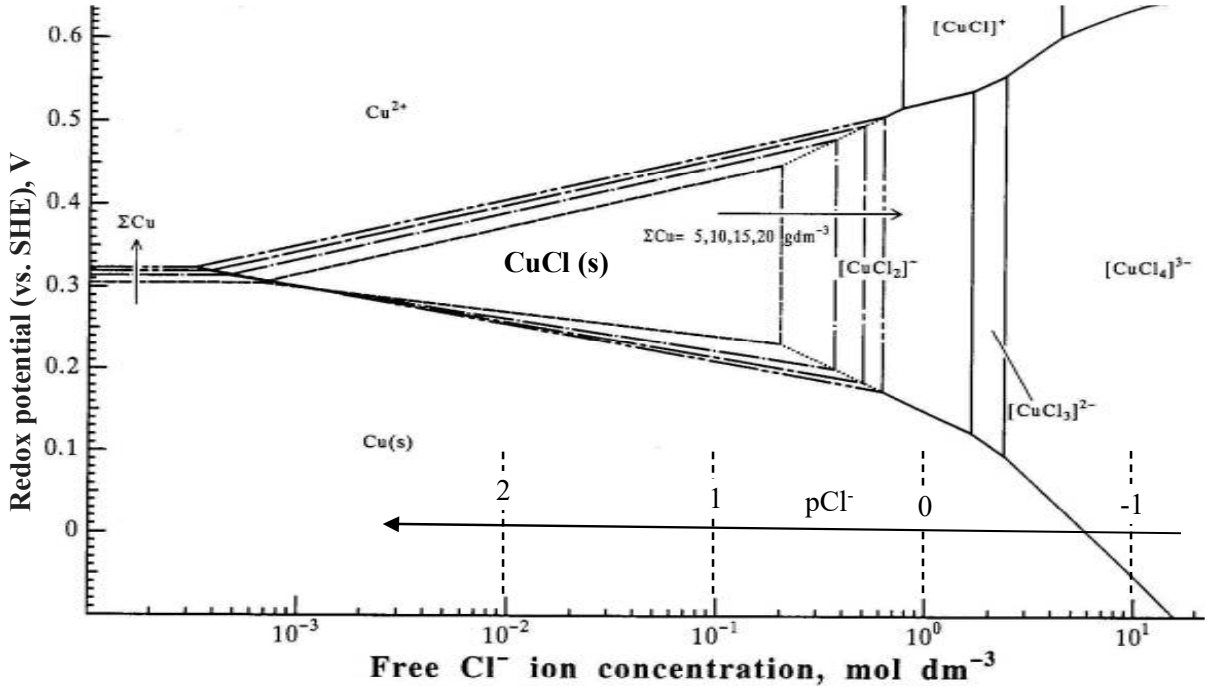

Figure 3. Stability of the Cu(I) species depending on the redox potential and the HCl concentration.

The distribution of dissolved iron among its usually possible oxidation states in acid solutions follows the same pattern as discussed for tin. The redox potential of the higher couple, Fe^{3+}/Fe^{2+} is higher (+0.741 V) than that of the lower Fe^{2+}/Fe couple (-0.44 V), even so, the difference in this case is considerably greater. The formation of chloro-complexes, although preferentially stabilizing the Fe(III) state, do not change the tendency, and Fe(II) is firmly stabilized in a com-proportionation reaction:

$$[FeCl_y]^{|3-y|sgn(3-y)} + Fe + (2x-y)Cl^- = 2[FeCl_x]^{|2-x|sgn(2-x)} \quad (2b)$$

if the solution is in contact with metallic iron. This is why the solution fraction of the pickling sludge contains dominantly Fe(II) ions. However, air can oxidize also the $FeCl_2$ solution, and the cathodic extraction may thus be interfered by the effect of Fe(III), although to a less extent than in the case of tin or copper. The major interference in this case can be the neutralization of the hydrogen ions at the cathode surface, as the redox potential of the Fe^{2+}/Fe couple is relatively low, significantly lower than that of the Sn^{2+}/Sn and the Cu^{+}/Cu systems.

The main cathodic processes of tin, copper and iron deposition from the chloride solutions of the examined secondary raw materials should not be disturbed by other metal ions. In the case of the lead-free Sn-Ag-Cu alloy, silver and copper are separated by the selective anodic dissolution tin, as the standard electrode potentials of the major accompanying elements are much higher (0.8 V for Ag^{+}/Ag and 0.5 V for Cu^{+}/Cu). However, in the cases of the PCB etching solution and the pickling liquor, the major dissolved impurity, zinc, should be removed before electrowinning.

Chloride solutions lend themselves to efficient purification by the possibility to separate dissolved metals in the form of chloro-complex ions [7]. In both waste solutions, generated by PCB etching, and by the pickling of steel objects – some of the zinc coated – contain mainly zinc to be preliminarily separated from the main component that can be electrowon at a high grade from the purified chloride

solution. A major advantage of applying anion exchange for the separation of metals dissolved as choro-complex ions is the controllability of ion stability. Fig. 4.*a* shows the differences in anion exchange distribution coefficients of zinc, copper and iron as function of the free chloride ion concentration. The distribution functions show, that the zinc impurity of the ~ 3 M HCl $CuCl_2$ spent PCB etching solution can be efficiently eliminated by selective absorption on a standard strongly basic – quaternary ammine type – anion exchange resin, while copper in the divalent form is not forming sorbable anionic complexes at any significant degree at this HCl concentration. This method of purifying the chloride solution can be developed into a comprehensive procedure where all the practical impurities are eliminated and ultra pure copper of extremely high value can be electrodeposited [16]. If copper is reduced to the monovalent state, the separation of zinc is cannot be executed perfectly, but those impurities which do not form anionic chloro-complexes can be separated in this way [17]. In a similar way, zinc can be virtually completely removed from the $FeCl_2$ – (~1M) HCl waste solution obtained from the preparatory step of hot dip zinc coating. This separation is still possible if iron is oxidized to the Fe(III) state at HCl concentrations below approximately 2 mol dm^{-3}. Similarly to the copper chloride solution, an comprehensive purification of the iron-chloride solution is also possible by a two-step complex anion-exchange procedure [18] and ultra pure iron can be produced, even from waste materials.

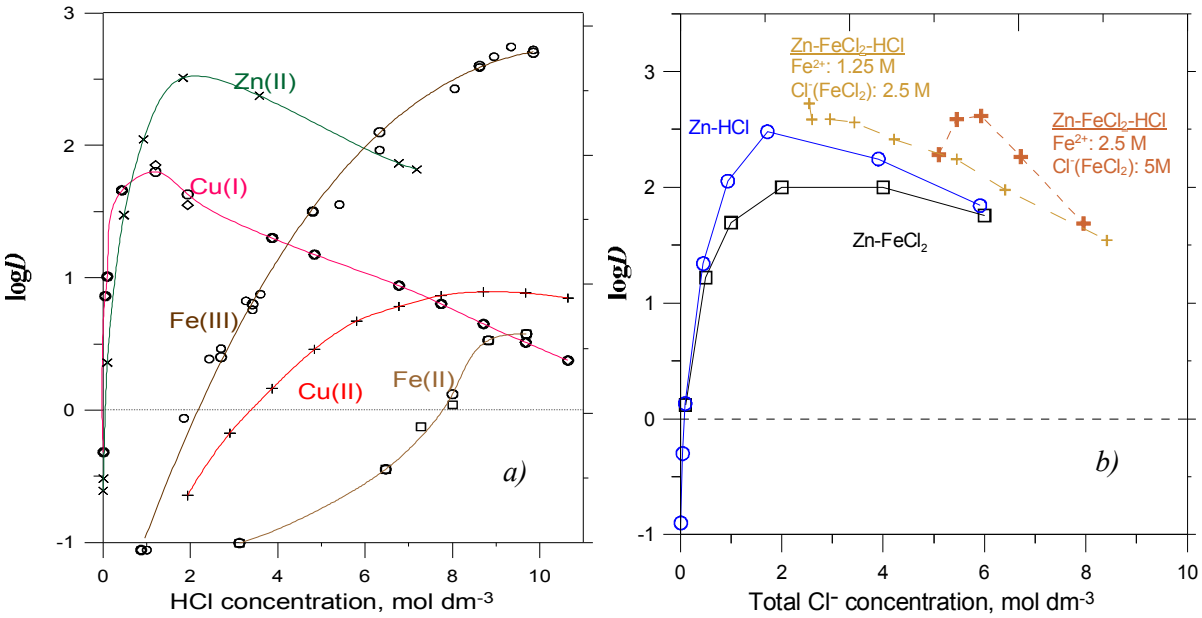

Figure 4. Anion exchange equilibrium distribution functions of zinc, copper and iron species in HCl (a) and in HCl-$FeCl_2$ solutions.

If chloride ions are supplied not only by the hydrochloric acid in the liquor, but the high concentration of the dissolved chloride of the main metal is also to be considered, the mean activity coefficient is affected. However, as proved by the results shown in Fig. 4*b*, the salt content does not change the tendency of anion exchange sorption, but as the relative activity of the chloride ions is reduced the intensive formation of the anionic complexes takes place at higher total Cl^- concentrations. Although the peaks of the distribution functions shift to the right if more of the chloride ions are supplied by dissolved salts instead of HCl, the relative tendencies determined in virtually pure HCl solutions still persist. Anion-exchange separations by chromatographic columns need to be optimized by laboratory experiments.

3. Experimental technique

As discussed above, the characteristics of the examined systems respond sensitively to changes in chloride and acid concentrations, or to redox potentials, thus detailed experimental work was needed for

defining the optimum or workable conditions in all cases. Despite all the difficulties of stabilizing the tin species in the acid solution, the main parameters of electrorefining the Sn-Ag-Cu alloy can be kept constant as tin recovered from the HCl-$SnCl_2$ solution at the cathode is dissolved virtually at the same rate from the anode cast from the remelted and skimmed soldering dross. However, in the cases of recovering copper from the spent PCB etching solution, or iron from the purified waste solution of the pickling operation applied before hot dip zinc coating inherently involves changing metal and acid concentrations during electrowinning.

The processes of tin extraction from the waste SnAgCu alloy by electrorefining solution is depicted schematically in Fig. 5. The formation of the Sn(II) species in an acid solution are in favour of lower specific electric energy consumption than in the case of depositing Sn(IV) species in alkaline solutions, although the possible com-proportionation reaction at the cathode reduces the current efficiency. It may however have a secondary beneficial consequence of refining the crystal structure deposited at the cathode. The diaphragm inserted in the generally used conventional cell (Fig. 5*b*) of 150 cm^3 dividable total volume near the anode surface serves to retain the fine particles of the generated anode slime. The balance of the tin concentration depends on the efficiency of the anodic and cathodic processes, which may be accompanied by subsidiary reactions of oxygen or hydrogen evolution, respectively [5], and also by oxidation at the surface of the electrolyte in contact with air. The electrolyte solution should be regularly conditioned not only because of the dissolved impurities of lower electrode potentials, but also for controlling the concentrations of the main components (Sn and HCl).

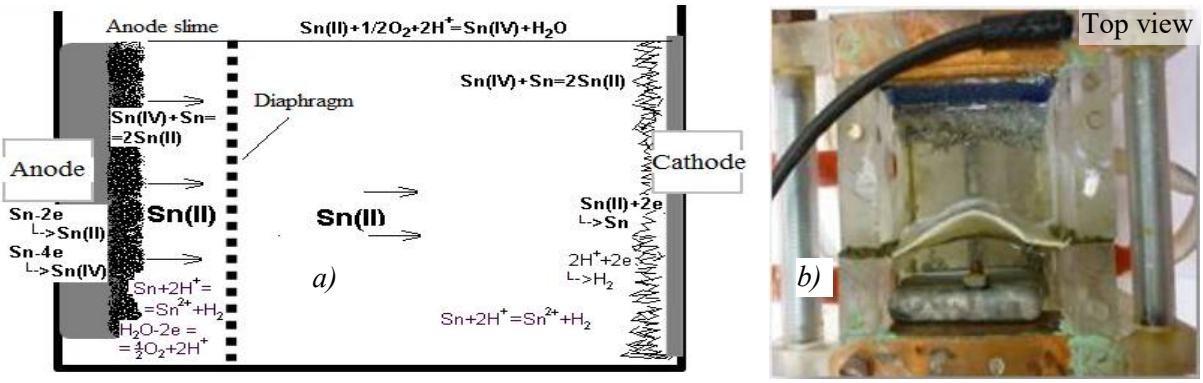

Figure 5. The processes (a) and the conventional cell (b) of electrorefining waste SnAgCu alloy.

The implementation of copper electrowinning from the spent PCB etching solution is technically more demanding. The processes and the main system parts are illustrated schematically in Fig. 6.

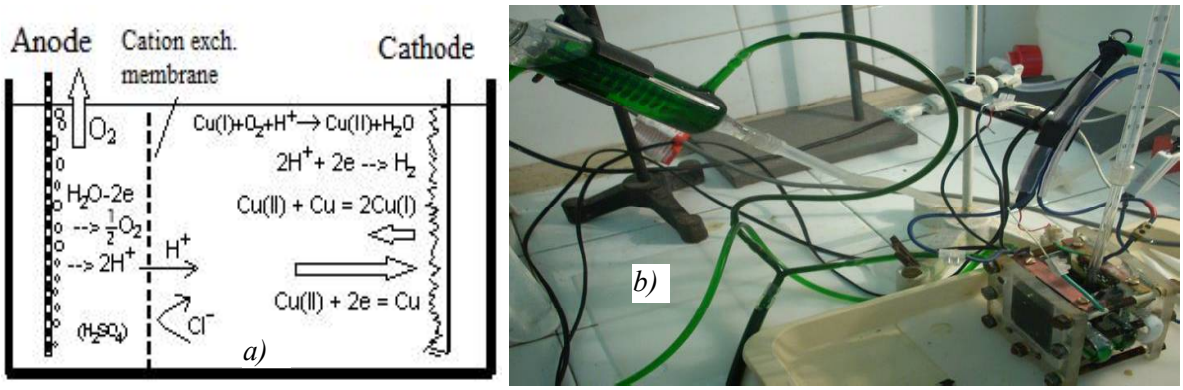

Figure 6. The processes (a) and the equipment (b) of copper electrowinning from PCB etching solution.

As the metal containing raw material is an aqueous solution (~160 g/dm^3 Cu, ~ 3 M HCl, 0.3 g/dm^3 Zn, and some other impurities at less than 30 mg/ dm^3 level), an inert (DSA) anode was used in an indifferent anolyte solution (~ 0.5 M H_2SO_4). Although the same cell was used as in the case of tin electrorefining, but now the diaphragm was replaced by a cation exchange membrane. The anode reaction involved oxygen evolution and generated H^+ ions. The latter were transported through the membrane which however blocked the chloride ions. The spent PCB etching solution – possibly after a preliminary anion-exchange purification – was fed into the cathode compartment. This catholyte was expected to get gradually depleted in copper and enriched in HCl. Due to the high electrode potential of copper, hydrogen could not evolve at the cathode. The solution remaining in the cathode compartment is fit for recycling to PCB etching or to be used for surface cleaning purposes before conventional coating procedures. The originally prevailing divalent copper species cause intensive cathode corrosion, and thus are gradually converted into Cu(I) by the com-proportionation reaction. The resulting re-dissolution of the deposited copper can be counteracted only by relatively high cathodic current densities. In an efficient operation with high currents applied to a relatively small cell, the electrolyte solution requires continuous cooling. This was implemented by pumping the solution through a heat exchanger where refrigerated water was also circulated.

In the case of extracting pure high purity iron from the purified $FeCl_2$-HCl waste solution, the system used for the copper extraction would not have been successful because the hydrogen ions transferred from the anode compartment through the cation exchange membrane to the cathode would soon become dominant in the cathodic process. Therefore, in the practical implementation of the process, a proton-blocking anion exchange membrane was inserted in the cell to retain the generated hydrogen ions in the anode compartment and the solution fed to the cathode compartment was conditioned for a preferably high initial iron concentration and a tolerable pH value. The optimum conditions were examined with synthetic test solutions and a graphite anode in the conventional layout of the 150 cm^3 cell. On the other hand, in the practical implementation, the danger of chlorine evolution at the anode was avoided by replacing the common inert material with a special hydrogen diffusion anode, fed by a controlled inflow of hydrogen gas. The anode reaction was then the oxidation of H_2 to form H^+ ions, as indicated in the schematic illustration of the cell in Fig. 7.

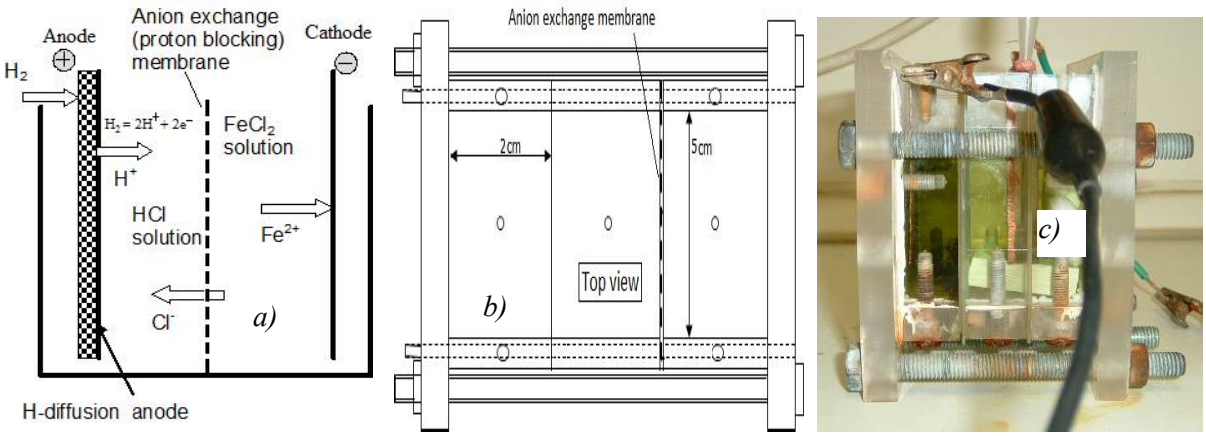

Figure 7. The processes (a) and the cell (b) of iron electrowinning from the purified pickling liquor, shown in operation (c).

In addition to the actual electrolysis experiments, the electrode processes of both tin and iron were investigated also by the standard three-electrode potentiodynamic technique. These experiments were run with varied concentrations of the targeted metal and HCl in the solutions in 5 mV/s potential steps at room temperature. The open cell was constructed of glass panes, but for testing the effect of the temperature, a special double wall cell was applied, connected to a thermostat bath with a peristaltic pump. The experiments were carried out with either stationary or stirred electrolyte, applying a magnetic

stirrer. A glass adapter ending in a Luggin-capillary of ~ 1 mm diameter connected a saturated calomel reference electrode (SCE) towards the center of the active working electrode surface. A computer with the IEMEAS 1.06 software recorded the current, supplied by an Electroflex EF 435C Potentiostat. The experimental setup is shown in Fig. 8.

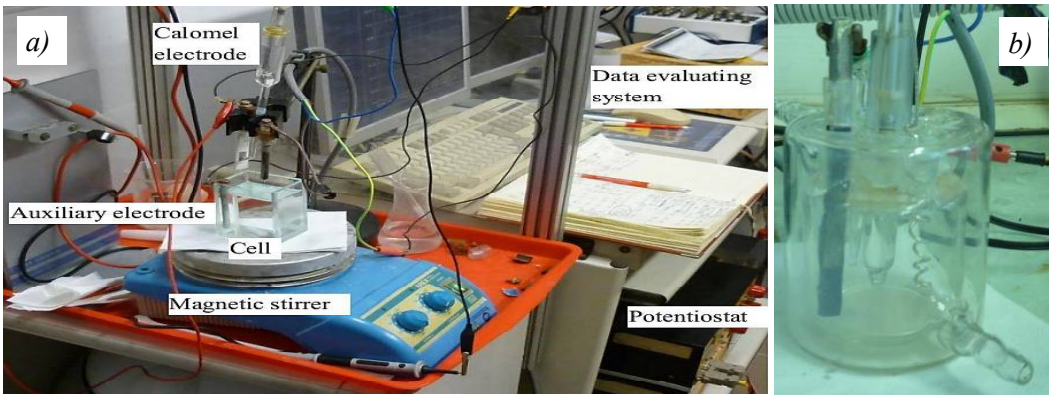

Figure 8. The equipment (a) and the special thermostated cell (b) of the potentiodynamic experiments.

4. Experimental results and discussion

4.1. Tin recovery from soldering dross by electrorefining

The advantage of applying acidic chloride versus sulphate electrolyte for tin extraction from the SnAgCu waste soldering alloy is justified by the comparison of the virtual – referring to the deposition of tin from the divalent state - cathodic current efficiencies. Figure 9 shows the effect of varied apparent cathodic current densities - referring to the geometric surface area of planar electrodes – and that of temperature. In order to moderate the growth of the cathode crystals, the current was modulated by the periodic current reversal (PCR) technique with the optimized forward/reverse time ratio of 20, and the current efficiencies are expressed as net values.

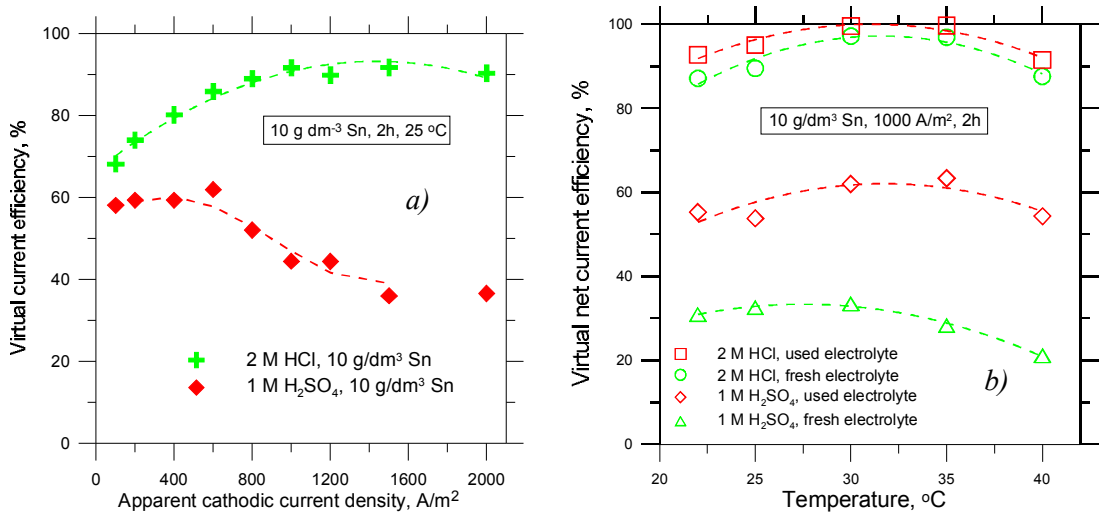

Figure 9. The effect of the increasing current density (a) and temperature at 1000 A/m^2 (b) on the virtual current efficiency in electrolyte solutions containing 10 g/dm^3 Sn and 2 M HCl or 1 M H_2SO_4.

Both the optimum current and the achieved current efficiencies are higher in the HCl based solution than those observed in the tested H_2SO_4 electrolyte of equal acidity. The optimum temperature may be around 30 °C, however, the change is so small that the use of room temperature can be a practical choice.

The effect of the temperature is complex. It enhances both the cathodic deposition and Sn(II) oxidation and also re-dissolution of the deposit by reaction. (1). The poor performance of the H_2SO_4 based system is probably attributable to the significant Sn(IV) concentration caused by the necessary application of aqua regia for the preparation of the electrolyte. The repeated use of a once run solution offers higher efficiencies because the Sn(IV) concentration may have been reduced during the first run. As the chloride electrolyte can be prepared simply by dissolving pure tin crystals in boiling and concentrated HCl, tin is in this case dissolved dominantly as Sn(II), as the com-proportionation equilibrium of reaction (1) prevails. It is also proved indirectly by the relatively slight difference in the current efficiencies between the two consecutive runs.

The changing conditions in the HCl electrolyte solution were examined by samples taken from both the cathode and the anode compartments at intervals when the mass of the produced cathodic deposit was also measured. As expected from the equilibrium considerations in Section 2, and shown in Fig. 10*a*, the total tin concentration was slowly but continually increasing both at the anode and the cathode sides, while the Sn(IV) concentration remained low and the HCl concentration was also found stable. This corresponds to the ideal mechanism based on the overall dominance of the generation and deposition of the Sn(II) species.

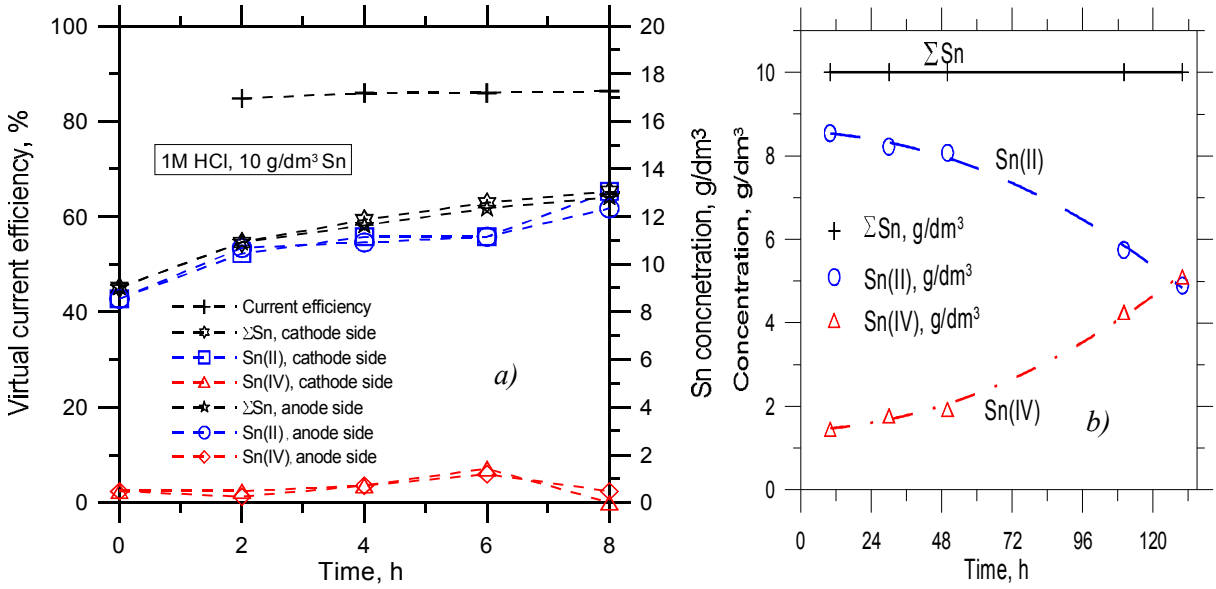

Figure 10. Changes in the current efficiency and tin concentrations during electrolysis (a) and (b) distribution of dissolved tin in 2 M HCl solutions during long time standing in contact with air.

The Sn(IV) species may arise either from a higher than ideal anode potential, from aerial oxidation, or both. The oxidation rate of dissolved Sn(II) species by air is shown relatively slow, demonstrated by the results in Fig. 10*b*. During the electrolysis the Sn(IV) concentration was found virtually stable and relatively low for a long (8 h) time of the experiment. However, the total tin concentration was gradually increasing. If Sn(IV) is generated at the anode it is converted into Sn(II) either at the anode slime layer containing finely divided tin particles, or at the cathode surface, where the tips of the fine tin dendrites can be re-dissolved. The overall increase of the total tin concentration is caused by aerial oxidation which could happen especially at the intervals when the operation was interrupted for removing and weighing the cathode. However as shown by Fig. 10*b*, this reaction is rather slow, hydrogen evolution at the cathode must have also taken place. This phenomenon can happen when the dendrites at the cathode surface grow too much and the current is mostly concentrated at the tips and edges of the crystals, where the local current density may increase considerably.

The cathodic reaction can be demonstrated by the relevant polarization curves shown in Fig. 11 presenting the results of investigations carried out in stationary electrolytes. By comparing the current densities obtained at the same cathodic overpotentials the effects of the solution composition can be evaluated. For comparison, Fig. 11*a* shows the reduction H^+ ions. It is seen that in the practical potential range, 1…2 M HCl still does not mean any interference in the cathode process. Fig. 11*b* and *c* show that below 20 g/dm^3 Sn concentration the cathodic reaction initially produces the expected exponential growth of the current but it is quickly stopped by the slow ion transport and a limiting current sets in. With further cathodic polarization the current sharply increases again without any limiting effect. This indicates the change into a rough cathode surface where large dendritic crystals are growing towards the counter electrode. Fig. 10*c* shows that at tin concentrations higher tin concentration than 20 g/dm^3 tin is deposited in a very rough dendritic form right from the beginning of the polarization run, thus the limiting current is not seen even temporarily.

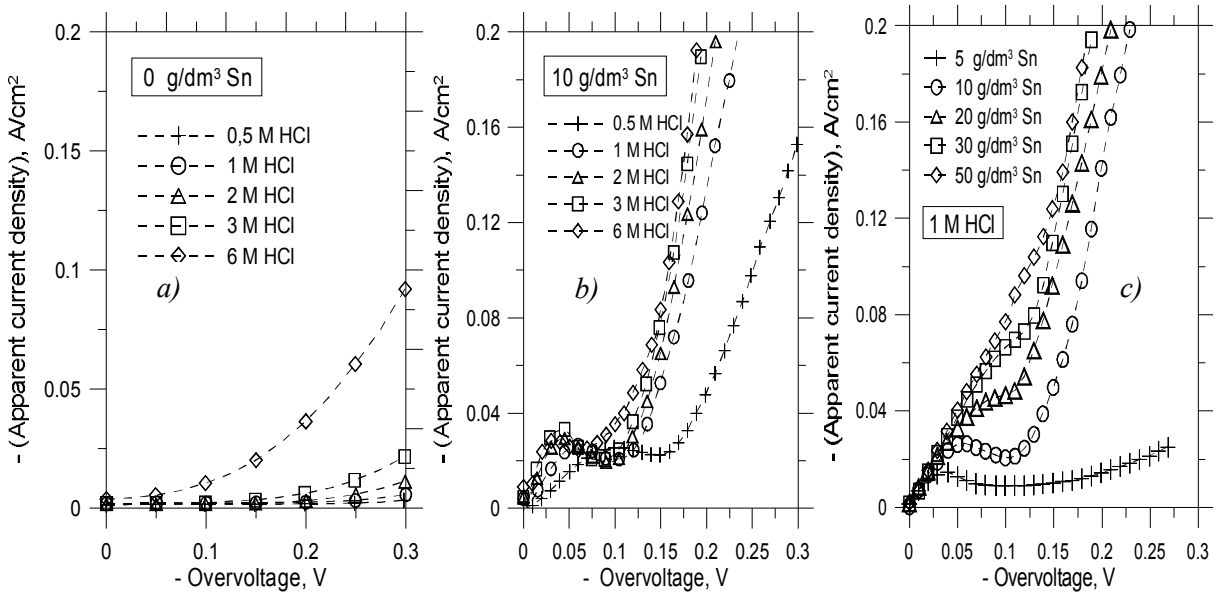

Figure 11. Cathodic polarization in stationary electrolytes containing different concentrations of HCl and Sn.

The Sn(II) reduction during the initial stages is strongly affected by stirring. Fig. 12*a* shows that a weak agitation pushes the limiting current clearly observed at 10 g/dm^3 Sn concentration in the stationary solution significantly higher indicating that the ion supply is effectively increased. With more vigorous agitation the temporary limiting current is completely eliminated and the large dendritic crystals projecting out of the cathode surface are seen growing directly in the beginning of the polarization run. On the other hand, the practical range of the anodic reaction is not enhanced by agitation, as show at the first sections of the curves in Fig. 12*b*. However passivation occurring at extremely high overvoltages is avoided until even higher potentials are reached. This can be interpreted by the more efficient removal of the Sn(IV) ions primarily formed – according to Fig. 1b - at as low electrode potential as ~ 0.1 V, corresponding to 0.2 – 0.3 V anodic overpotential on the tin electrode. The enhanced transport can prevent the accumulation of Sn(IV) ions and the formation of stannic acid precipitation.

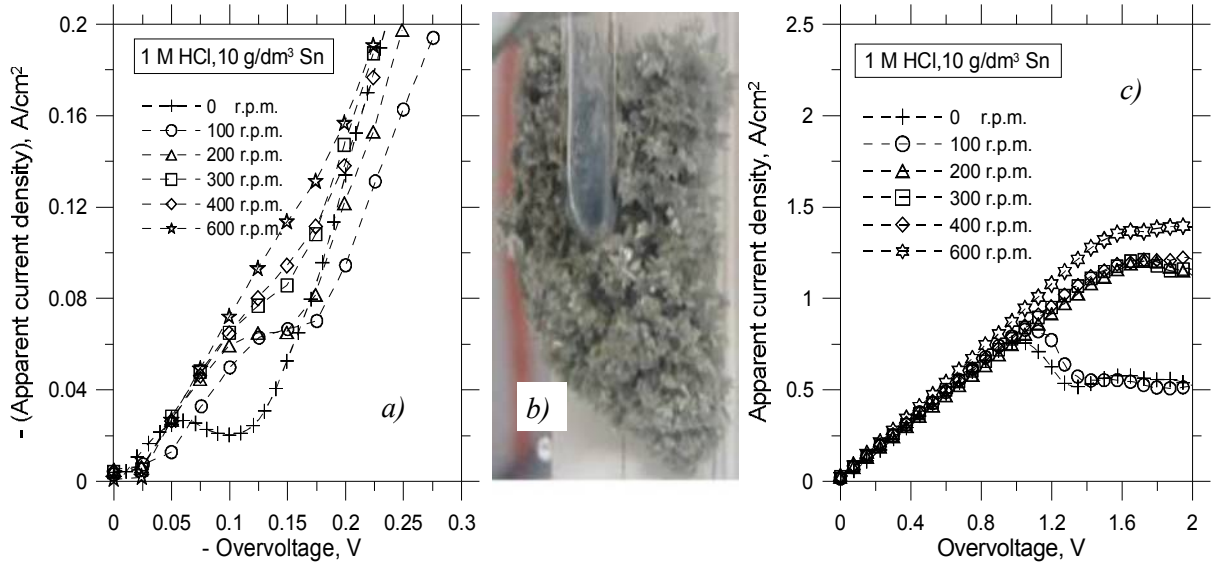

Figure 12. The effect of increased stirring on the polarization curves in electrolyte solutions of 10 g/dm^3 Sn and 1 M HCl a) – cathodic current, b) rough dendritic crystals grown, c) – anodic current.

Tin is deposited with a rough morphology at the cathode from both types of the electrolyte solutions. The form of electrocrystallization in stationary chloride electrolytes depends on the tin concentration and the applied current density, as shown in the array of macro photographs of Fig. 13, arranged according to conventional system [19].

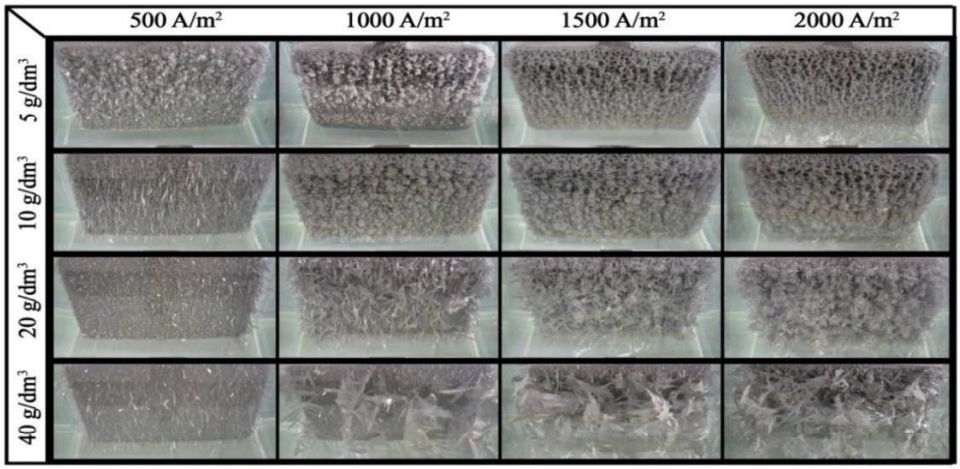

Figure 13. Cathodic deposits obtained after 5 minutes of electrolysis by using different tin concentrations in the 1 mol/dm^3 HCl solutions and various apparent current densities

The fast growing dendritic crystals could easily reach the anode, but at high current densities, as the front of the crystals get far from the cathode substrate, the highly concentrated local current causing first powder deposition and then hydrogen evolution. Even the diaphragm cannot prevent the crystals growing into the anode surface, which physically terminates the effective electrolysis. In order to avoid such severe circumstances, without the continuous supervision of the cell, we have devised automated electromechanical systems periodically or continuously compressing the rough cathodic deposit [6]. The rough crystals are compressed by a perforated pressing plate moving periodically between planar electrodes (Fig. 14*a*), or by a pressing rod touching the surface of a continuously rotating cathode of

cylindrical shape (Fig. 14*b*). The preferred electrode processes can be assured by controlling the actual electrode potentials, which can be critical especially for the anodic dissolution.

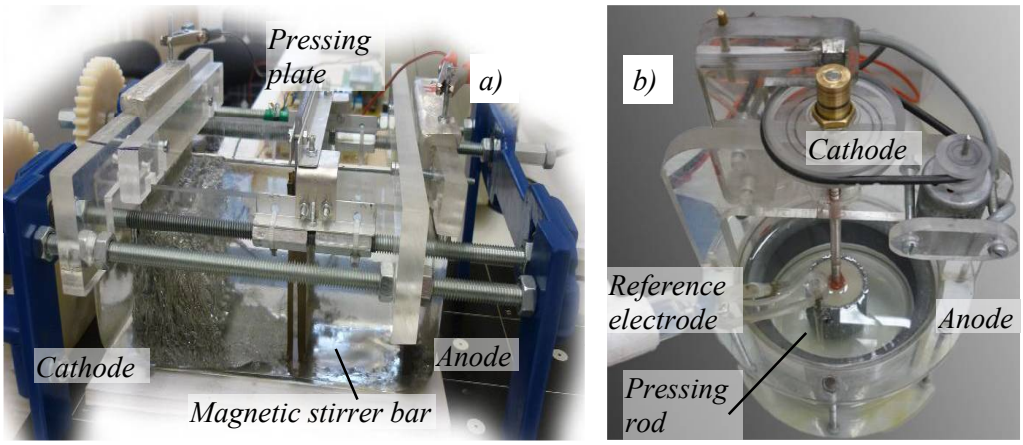

Figure 14. Periodical (a) and continuous (b) cathode compression in electromechanical cells.

Tin was extracted with more than satisfactory purity. The main impurity, copper is practically retained in the anode slime, together with silver, and the rest of the impurities are also separated. The efficiency of purification can be assessed by comparing the compositions of the anode made of the raw material and the produced deposit at the cathode. Table 1 shows the impurity concentrations in the cathode deposits corresponding to the process characterized by Fig. 10*a*.

Table 1 - The compositions of the impure anode and the purified cathode material

Sample	Concentration, %							
	Ag	Bi	Cu	Fe	Ni	Pb	Sb	Total
Anode	0.0805	0.0414	1.9605	0.0050	0.0004	0.0187	0.0367	2.1432
Cathode (8h)	0.0004	0.0004	0.0063	0.0004	0.0000	0.0036	0.0003	0.0115

4.2. Copper recovery from the PCB etching solution

The effect of copper dissolution predicted by the equilibrium study of reaction (2) was tested by immersing copper plates into solutions of varied $CuCl_2$ and HCl concentrations. The highest rate of dissolution was found at a Cu concentration of 150 g/dm^3 and the highest examined HCl concentration of 3 mol/dm^3. This composition corresponds to the raw solution obtained from PCB etching, therefore high initial rates of cathode corrosion was expected. The expectations were proved by the low current efficiencies seen in Figure 15.

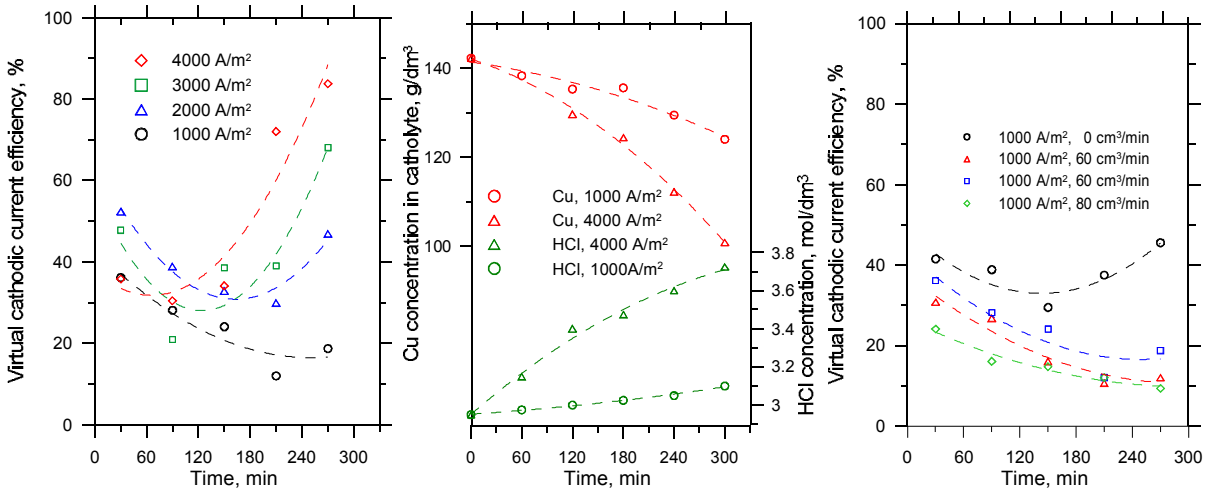

Figure 15. Cathodic current efficiency (a), catholyte composition (b) as functions of electrolysis time, and the current efficiency as a function of the flow rate (c) of the spent PCB etching solution.

The initial decrease in the current efficiency in Fig. 15*a* can be attributed to relatively strong roughening of the cathode surface just after start, enhancing the corrosion process, while the rate of deposition at the set current is constant. This tendency is later reversed as the Cu(II)/Cu(I) concentration ratio decreases by the reaction of the cupric ions with metallic copper described by Eq. (2). Thus the cathode corrosion subsides. The green $CuCl_2$-HCl solution turns dark brown, than light brown during the course of the electrolysis. This indicates the increasing Cu(I)/Cu(II) concentration ratio, which – at a certain range – may result in the formation of mixed Cu(I)-Cu(II) chloride interaction complex species [20,21].

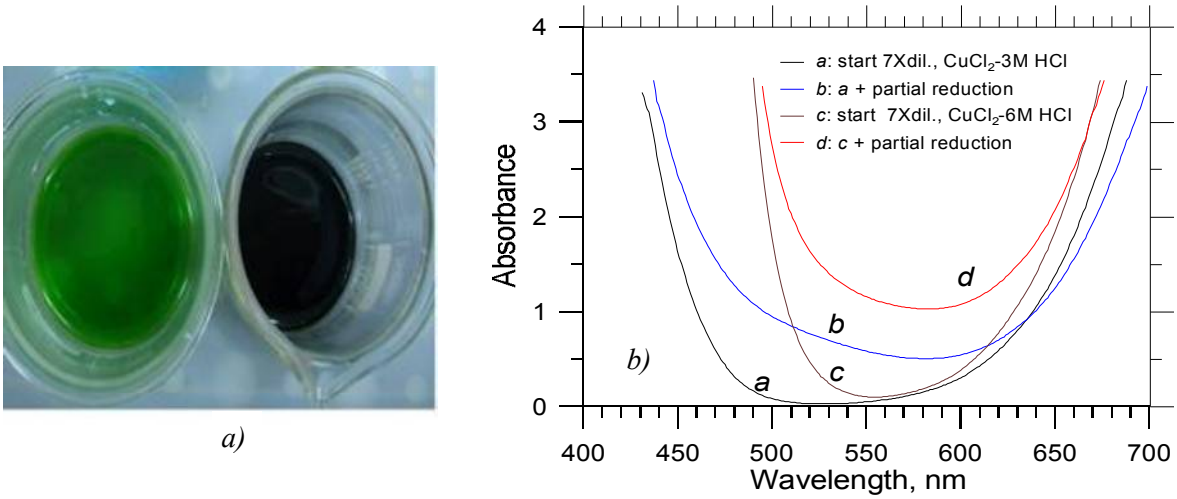

Figure 16: The initial change in the colour of the PCB etching solution during electrolysis (a) and the change in light absorption spectra (b) of the starting and the partly reduced solution after dilution.

In order to record the absorption spectra, the PCB etching solution was examined directly – only diluted with HCl solutions and – and also after partial reduction with zinc powder. Comparison of the relevant pairs of the spectra in Fig. 16*b* show that the light absorption in the 500~600 nm wavelength range is increased by converting some part of the Cu(II) into Cu(I). The increased light absorption arouse even if zinc powder even removed some of the total copper content from the solution, but after the particles were coated by copper, reaction (2) could be considered as the major process. The interaction complexes are finally decomposed as the Cu(II) content gets virtually consumed and the colour of the solution is

getting simultaneously lighter. In the meantime, the copper content in the cathode compartment is gradually replaced by the hydrogen ions generated at the anode are transferred through the membrane, as shown in Figure 15*b*. The unfavorable effect of forced electrolyte circulation – enhancing the chemical reactions of cathode corrosion - on the current efficiency is demonstrated by Fig. 15*c*. Nevertheless, the electrolyte has to be circulated through the heat exchanger for cooling, especially if higher current densities – counteracting copper re-dissolution - are applied.

The distribution of copper among the Cu(II) and Cu(I) species may have a significant influence - beyond the strong effect on the current efficiency – also on the morphology of electro-crystallization. The photo of Fig. 17 shows the deposit obtained by running the cathode with the highest examined current density for 8 hours.

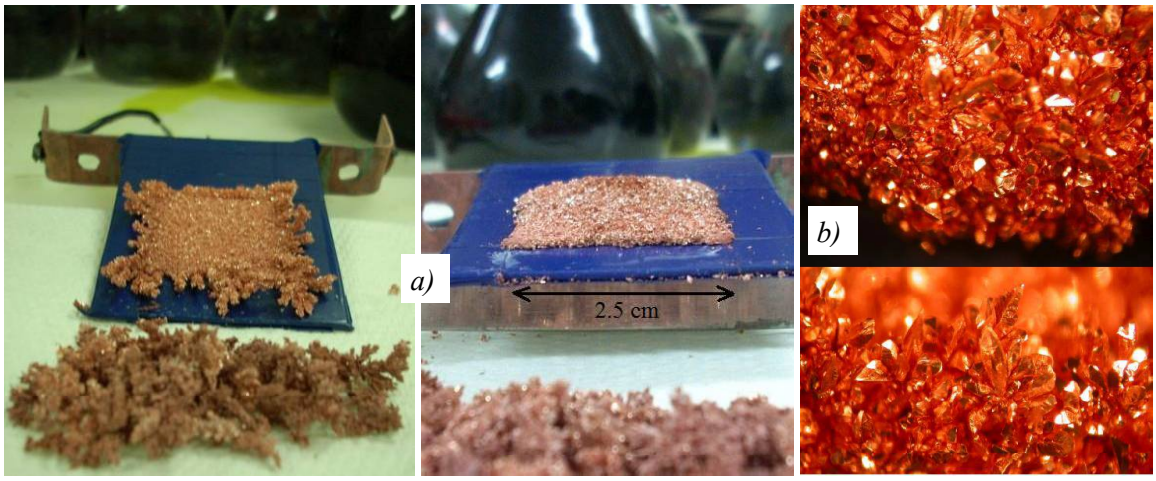

Figure 17. The photographs of the cathode obtained with 4000 A/m^2 apparent current density after 8 h electrolysis time (a) and the microphotographs of the crystals at a corner of the main body (b).

During the first few hours of the long electrolysis run, relatively large dendrites were growing at the edges of the active cathode surface (shown removed in Fig. 17*a*), but later the type of deposition seemed to change from the field oriented isolation type to a more uniform base oriented reproduction. It may result from a decreasing ratio of the actual and the limiting current densities [19], which is possible if the mechanism of cathodic deposition is facilitated by the excess of the monovalent copper species.

The recovered copper is of higher than technical (< 99.9 %) purity. Only zinc (~370 ppm) and iron (~10 ppm) can be considered as practical impurities. Electrowinning from the PCB etching solution could offer purification ratios – referring to relative concentration in the solution vs. tin the cathode metal) for these elements in the range of 5 – 10. To achieve an even higher purity in the copper produced, a simple anion exchange can be applied before electrowinning directly to the raw solution as demonstrated by the elution curves and the process photographs of Fig. 18. According to the equilibrium results shown in Section 2, Zn should be efficiently retained in the anion exchange resin bed during the steps of loading the raw solution and the subsequent rinsing with 3 M HCl, while copper in the divalent state should run through the column. The relatively low leakage of Zn overlapping the copper elution peak is a result of the high total chloride concentration, as copper chloride contributes 5 mol/dm^3 free Cl^- in addition to the ~ 3M HCl concentration in the raw PCB etching solution. According to the equilibrium distribution function of Fig. 4*a*, the anion exchange distribution coefficient of zinc is an order of magnitude lower in 8 M Cl^- solution than at its maximum in 2 – 3 M free Cl^- ion concentration. This effect is however useful in retaining also Fe(III) in the resin bed while most the copper content is eluted. The increased total Cl^- ion concentration did not hinder the elution of Cu(II). This can be interpreted with the still relatively low maximum distribution coefficient of Cu(II) and kinetic factors. In this case a faster flow rate of the solution through the column may be advantageous. Although the activity coefficients influencing the chloro-complex formations are not exactly the same as in pure HCl

solutions, the equilibrium distribution functions determined in HCl media can be used for devising separations and the fine adjustments must be made according to elution tests. In this case the directly achieved relatively good partial separation of Zn and Fe from copper was satisfactory, thus the preliminary purification of the waste PCB etching solution was not optimized further.

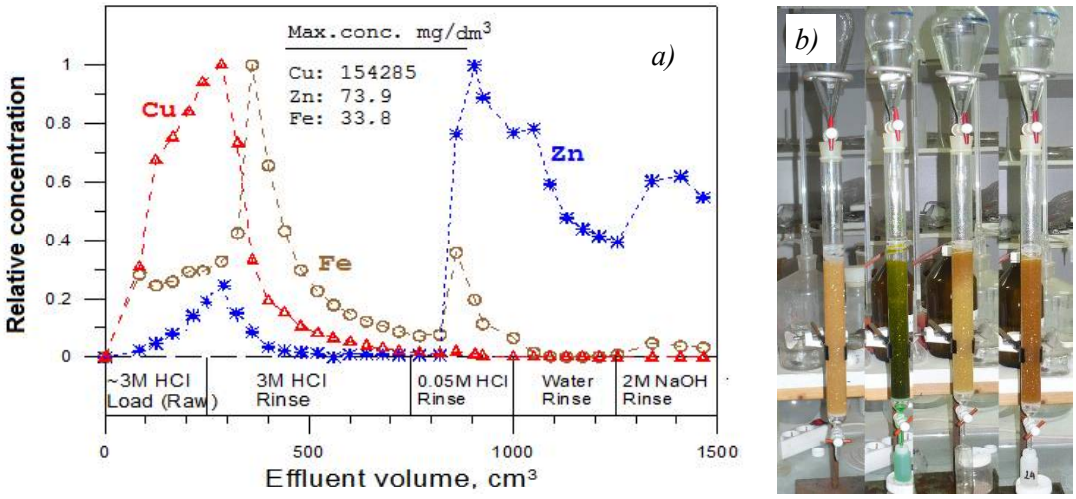

Figure 18. The elution curves (a) and photographs (b) of the direct anion-exchange purification steps of the PCB etching solution.

4.3. *Iron recovery from the spent pickling liquor from zinc coating*

The relatively novel, but technically mature and reliable hydrogen diffusion anode [22, 23] was found working with good efficiency [9]. However, the hydrogen ions are challenging competitors in the $FeCl_2$-HCl solution for iron electrodeposition it was not enough to block their transfer from the anolyte by applying the proton-blocking anion exchange membrane, but the initial HCl concentration of the catholyte also had to be adjusted after the anion exchange separation of zinc. For the stability of the solution and for economical reasons, however, the neutralization of the solution should be limited to the required minimum degree. Therefore it was of prime importance to examine the effects of pH and other important factors influencing the cathodic current efficiency. These experiments were carried out in the conventional cell with usually stationary electrolytes and copper cathodes - of 6.25 cm^2 active surface area - for times allowing the passage of 350 As electric charge for each measurement. The critical effect of free acid concentration at a relatively low current density is demonstrated by the results in Fig. 19*a*. The significance of the applied current efficiency is demonstrated by the results in Fig. 19*b*. In order to see the reasons of lost current, the iron deposits were re-dissolved in the electrolyte solution for the same time as the electrolysis was run. The ratio of the theoretically expected iron mass, and the re-dissolved mas was compared to the total deposit obtained, thus the overall and the partial current efficiencies were expressed. The latter could be attributed to only chemical cathode corrosion. It is seen that at low initial current densities the chemical re-dissolution of the deposited iron is less significant in causing the current loss than hydrogen evolution, because in the applied relatively short electrolysis time (45 min at 200 A/m^2) the cathode surface remained relatively smooth. On the other hand, with an intensive electrowinning at more than ten times higher current densities the deposited iron forms a rough porous cathode surface where the actual surface area is increased and hydrogen evolution stops. In this case the relatively slow chemical re-dissolution remains as the practical cause of current loss. The current efficiency of iron deposition is strongly increased by increasing the Fe(II) concentration, as shown by Fig. 19*c*, corresponding to reported results in earlier literature [24,25]. It has serious practical consequences in defining the limits of the iron electrowinning operation.

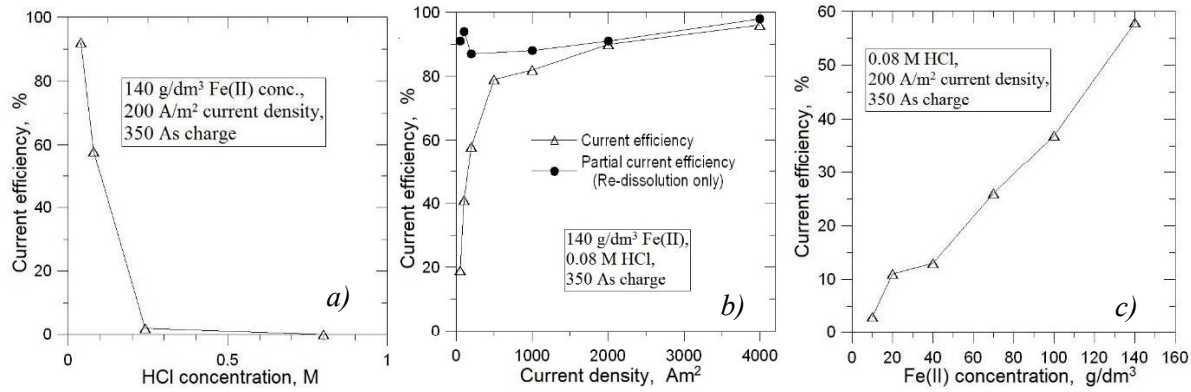

Figure 19. The current efficiency of galvanostatic iron deposition from stationary electrolytes as a function of) HCl concentration; b.) current density; c) Fe(II) concentration at 20 °C.

The agitation of the electrolyte was found strongly reducing the achievable current efficiency. This effect indicates that the transfer of the iron ions in the 140 g/dm^3 Fe(II) solution is sufficiently fast, and stirring mainly increases the re-dissolution reaction and even enhances the kinetics of hydrogen evolution, therefore stationary electrolytes can be recommended. The effect of temperature was examined with a low (200 A/m^2) current density and 140 g/dm^3 Fe(II) - 0,08 M HCl stationary electrolyte. Similarly to the case of copper electrowinning from the PCB etching solution, the effect of temperature is not significant here. However, here the current efficiency had a minimum at 40 °C, while 25 °C and also at 60 °C proved similarly advantageous. This can be attributed to the similarly increased rates of iron diffusion and re-dissolution and to the similar effects of temperature on the deposition kinetics of Fe(II) and hydrogen.

The results of the main potentiodynamic experiments indicate the similar deposition potentials and mixed polarization characteristic of Fe(II) and hydrogen cathodic reduction. Figure 20*a* shows the short term (5s) polarization curves determined in solutions containing 0 or 140 g/dm^3 iron as functions of HCl concentration, temperature and Fe(III) concentration. With a high HCl concentration in the solution, the electrode surface (polished after the previous run) is chemically attacked, and the iron ions locally concentrated around the electrode can be initially precipitated, resulting in the initial rise of the polarization curves. At higher potentials, however the regular deposition of iron ions from the bulk solution develops mixed with the evolution of hydrogen.

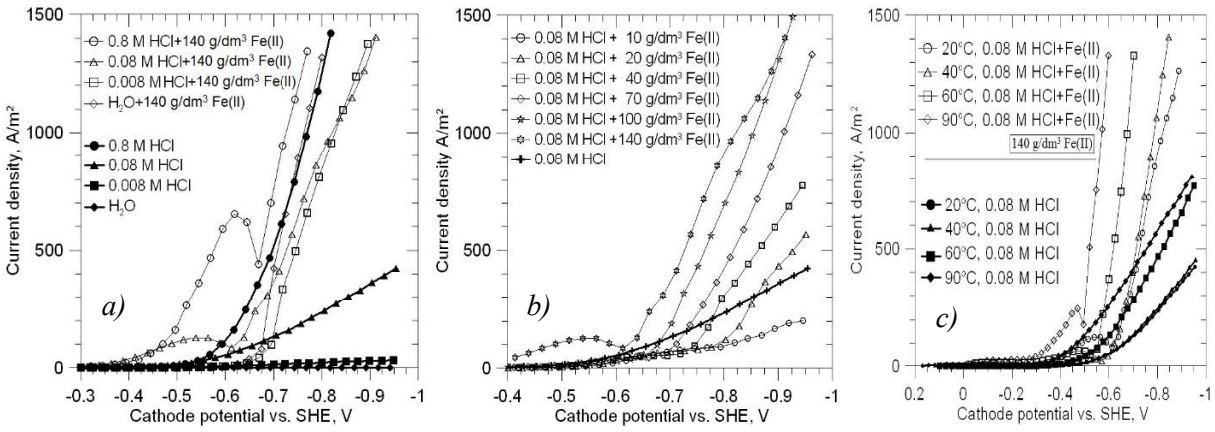

Figure 20. Polarisation curves obtained in solutions of different a) HCl concentrations; b) Fe(II) concentrations and c) temperatures.

As shown by Fig. 20*b*, increasing the iron concentration results in higher currents. Comparing these current densities to those corresponding to only hydrogen evolution shows that with little $FeCl_2$ added

to the 0.08 M HCl solution, the hydrogen evolution is rather depressed. It may be attributed to a decrease of the activity coefficient. With a low Fe(II) concentration (10 g/dm^3) a limiting current can be observed, but at increasing Fe(II) concentrations, a generally intensive iron deposition starts at gradually lower potentials. The overall current still may contain a significant component from H_2 evolution. Increasing the temperature brings the deposition potentials of both iron and also of hydrogen considerably lower.

In order to interpret the nature of the initial current waves, polarization experiments were carried also with varied delay times, stirring speeds, and with the addition of hydrogen peroxide or in zinc containing solutions. These results are shown in Fig. 21. Stirring generally increases the cathodic currents at a given potential. With longer delay times at the potential steps before recording the current, the polarization curves are shifted to higher, showing that the surface of the electrode is getting rougher as more iron is deposited. The addition of H_2O_2 resulted in higher initial current waves because it renders the acid solution more aggressive. The initial current wave is present also in the case of the $ZnCl_2$-HCl solution, which proves that this phenomenon is not related to a reduction of higher oxidation states.

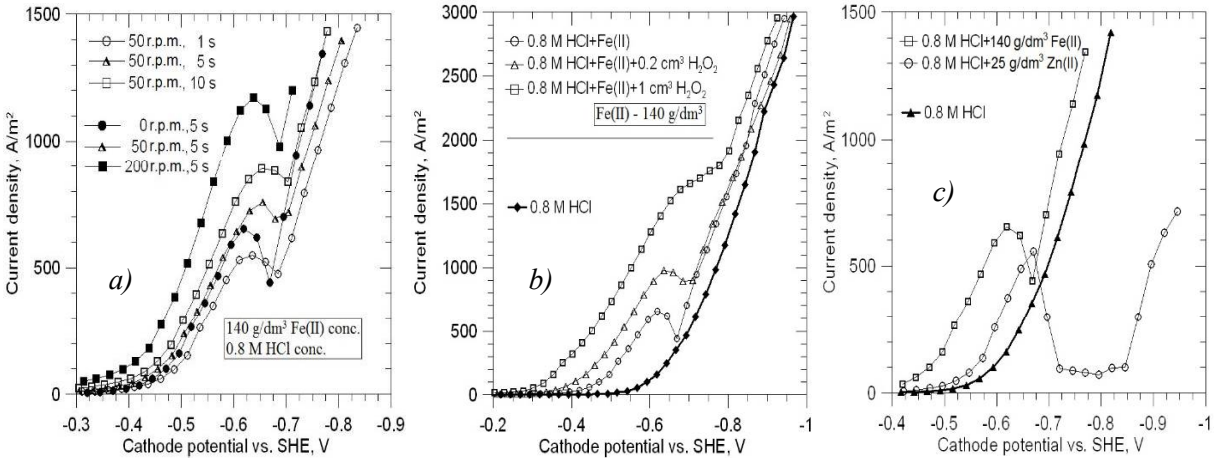

Figure 21. Polarisation curves of Fe(II) reduction with different a) delay times, b) H_2O_2 additions and c) metals added.

The capacity and the performance limits of the hydrogen diffusion anode were primarily investigated by the potentiodynamic method. Fig. 22 shows the anodic polarization characteristics at different H_2 gas flow rates, HCl concentrations and temperatures.

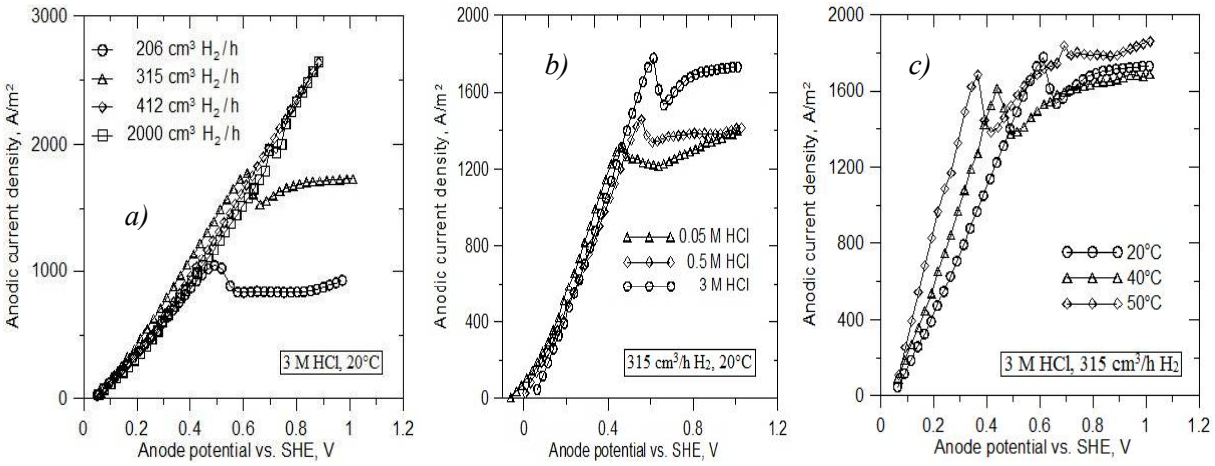

Figure 22. Polarisation curves of H_2 oxidation with different a) gas flow rates, b) HCl concentrations and c) temperatures.

As demonstrated by the results in Fig. 22*a*, the gas supply does not change the characteristics of the anode, but quite naturally, it limits the maximum currents density. Figure 22*b* proves that the HCl concentration may have neither any effect on the anodic process, however the limiting current is increased slightly by this factor too. The applied temperature (Fig. 22*c*) does not change the dissolution potential of hydrogen, but decreases the polarization resistivity of the hydrogen diffusion electrode.

According to the results of the galvanostatic and the potentiodynamic investigations a solution containing 140 g/dm^3 Fe(II) and 0.08 M HCl was treated in the laboratory cell equipped with the hydrogen diffusion anode fed with a H_2 stream of ~400 cm^3/h in a compartment separated by an anion-exchange membrane from the copper cathode plate operated with a current density of 1500 A/m^2 for 13 hours continuously. The performance characteristics are summarized in Fig. 23.

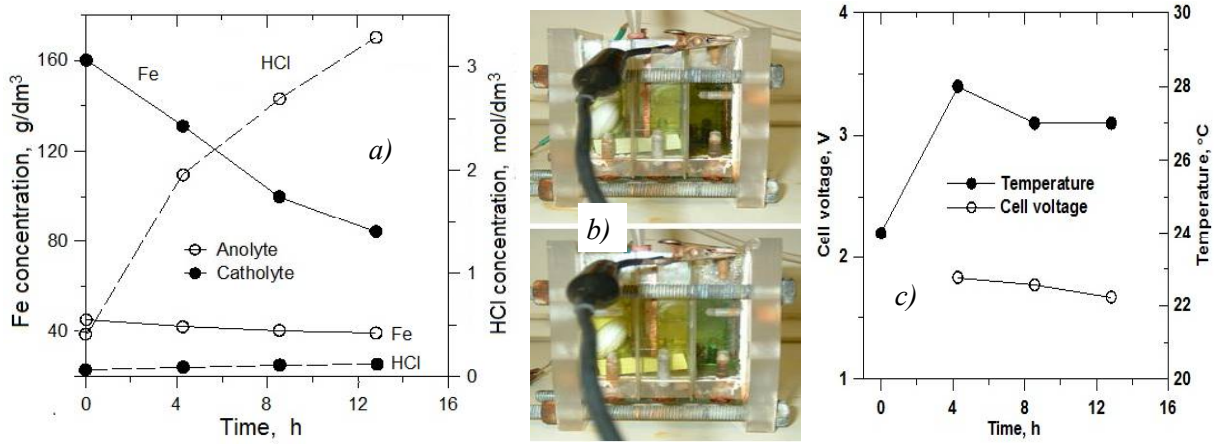

Figure 23. The performance characteristics of the cell with a hydrogen diffusion anode and anion-exchange membrane in time (a – concentrations, b – solutions, c – temperature and voltage).

The special electrowinning cell could provide the required processes for recovering iron and regenerating HCl with stable performance. After 13 hours though, the electrolyte should be replaced, because the cathodic current efficiency may be decreased by the low Fe(II) concentration reached, as suggested by Fig. 19c. If it implies the consumption of hydrogen ions from the cathode compartment, the precipitation of $Fe(OH)_2$ may appear. However, the analysis of the catholyte did not show any significant consumption of hydrogen at the cathode, even when half of the original iron content was removed from the solution. Thus the laboratory cell demonstrated that this special membrane-

electrowinning is capable of reducing the iron concentration of a spent pickling liquor to ~ 80 g/dm^3 and increasing the HCl concentration to ~ 3.3 M by consuming ~ 0.2 kWh electricity and ~ 0.025 USD worth of hydrogen for the treatment of one litre solution.
The operation however requires the preliminary removal of zinc from the raw solution. According to the anion exchange equilibrium results shown in Fig. 4*b*, the spent pickling solution containing ~ 100 g/dm^3 iron dissolved as Fe Cl_2, and some HCl contains enough free chloride ions to convert zinc into the $[ZnCl_x]^{(x-2)-}$ type anionic complex species. Therefore it can be directly fed into a column containing a strongly basic anion-exchange resin bed. However, because of the high zinc content, it is practically required to remove most of the zinc in a preliminary batch anion-exchange step because the capacity of the resin bed in the column is rather limited. Subsequently, zinc can be then completely eliminated from the pre-purified solution by the ion chromatographic separation [26]. The latter step is demonstrated by the elution curves shown in Fig. 24*a*. This operation can eliminate Zn from The $FeCl_2$ solution efficiently and as an added benefit, the copper impurity is also removed, although with less efficiency. However this chromatographic separation is very sensitive to the applied flow rate [26]. With a fast flow of 10 bed volumes per hour, zinc is hardly sorbed, as shown in Fig. 24*b*, and a great proportion is eluted together with the non-sorbed Fe(II) species. The efficiency of the fine Zn-Fe separation by ion chromatography could be enhanced significantly by reducing the flow rate to ~ 1 bed volumes per hour (1 BV/h), corresponding to the results in Fig. 24*a*.

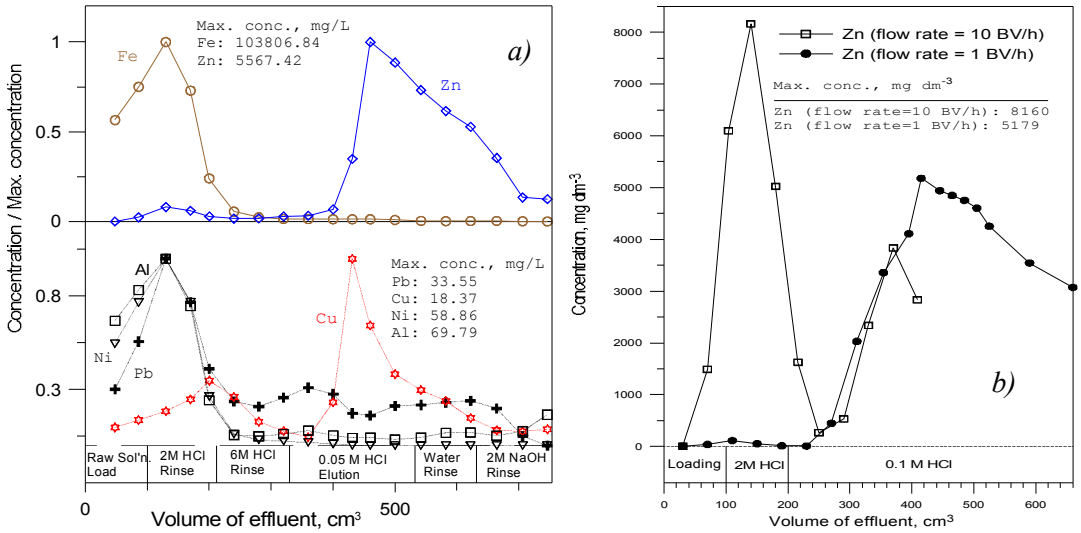

Figure 24. Elution curves of anion exchange separation of Zn from the spent pickling solution.

The used resins saturated with zinc can be regenerated by rinsing with e.g. 0.05 M HCl solution, as shown in Fig. 24*a*, resulting in the elution of Zn. This step can be followed by a conditioning procedure by converting the resin into the hydroxide, then again fully into the chloride form. The resin bed is conditioned in the column and the resin from the batch step is conditioned in a similar batch process. After de-zincing the iron effluent is fit for the membrane electrolysis. The residual electrolyte from the cathode compartment can be used for pelletizing in the ironmaking industry. The final anolyte is suitable for recycling to the pickling operation of the galvanizing industry.

5. Conclusions

Some special industrial waste materials can offer excellent sources of important metals, but the conventional technology is either un-economical, not easily attainable or simply inexistent. In the latter case, some potential secondary raw materials usually end up as deposited waste, thus losing their inherent value and causing environmental burden. The proposed chloride based hydro-electrometallurgical methods, on the other hand, offer novel solutions for extracting the valuable metals with little investment and low operating costs even for small scale businesses. This approach opens a

new way for the processing of lead-free soldering dross. The chloride solution makes it possible to omit the expensive components of the conventional sulphate based electrolyte allowing also to achieve high efficiency and super purity tin, beside valuable by-products. In other cases – like the spent solutions from PCB etching or pickling of steel structures before zinc coating – invite chloride hydro-electrometallurgy as a direct approach, as these raw materials are already solutions of metal chlorides and hydrochloric acid. The efficient electrowinning of pure metals from these two waste solutions can be implemented in membrane cells to prevent chlorine evolution while the acid is regenerated and the main metal is deposited. The chloride system also favors solution purification by the anion exchange technique. The processes were devised by theoretical and experimental equilibrium studies and optimized by laboratory scale potentiodynamic, galvanostatic experiments, as well as performance tests.

Acknowledgement
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